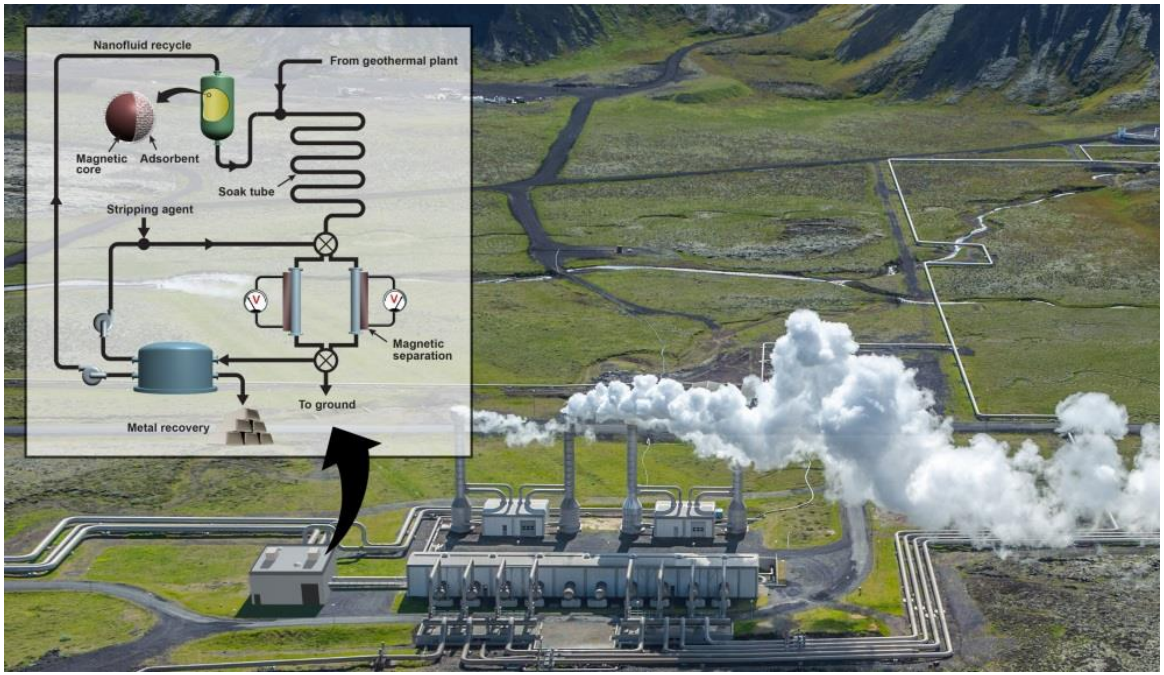
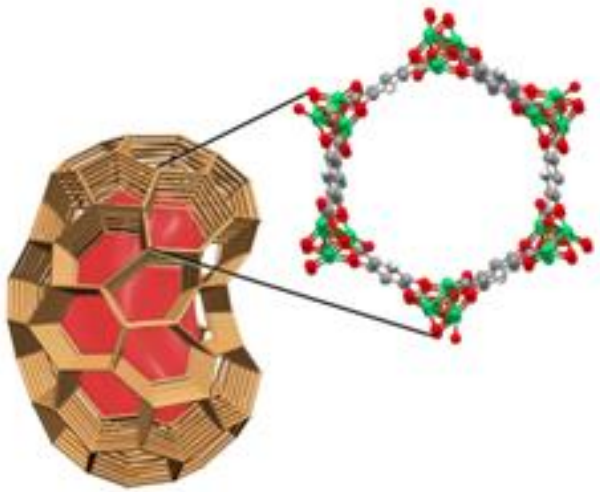


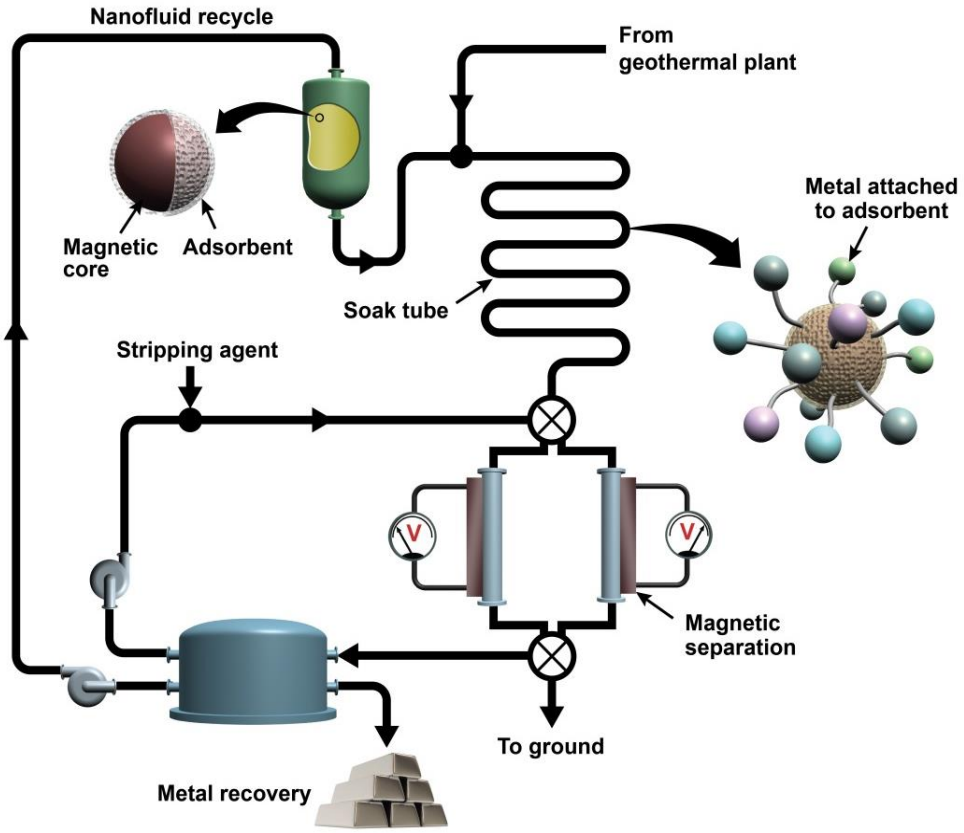


Magnetic Partitioning Nanofluid for Rare Earth Extraction from Geothermal Fluids

B. Peter McGrail
Pacific Northwest National Laboratory
Specialized Materials and Fluids for Power Plants

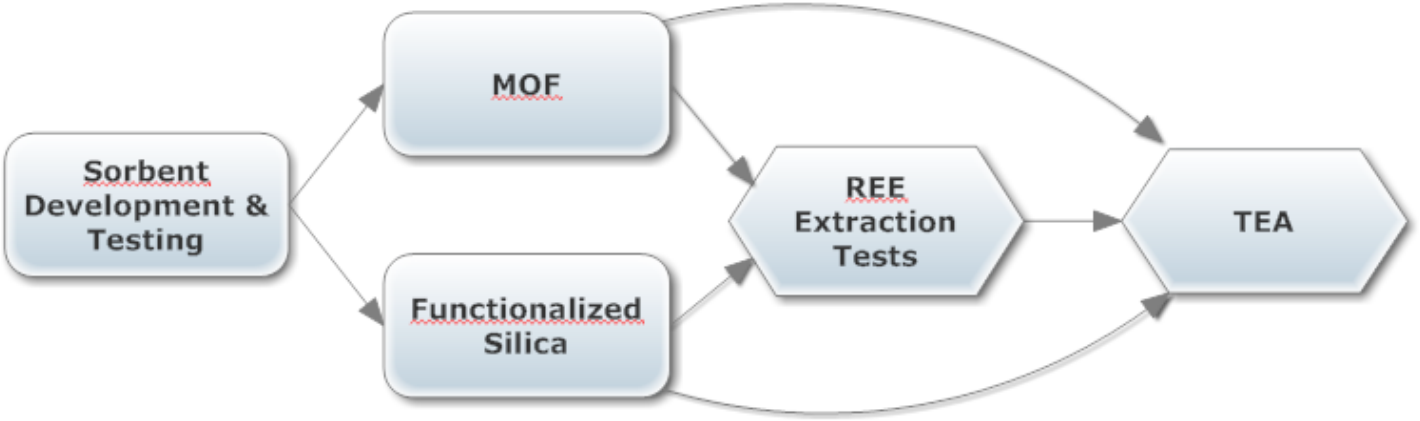
Relevance/Impact of Research

- Nanoparticles provide high surface area and excess of chelating sites for REE extraction at low (ppb) concentrations
- Use of nanofluid avoids packed beds with large pressure drop, size, capital, and operating costs
- Magnetic core allows for simple and low energy use separator
- Achieve 90% REE removal efficiency at production cost less than half present commodity pricing



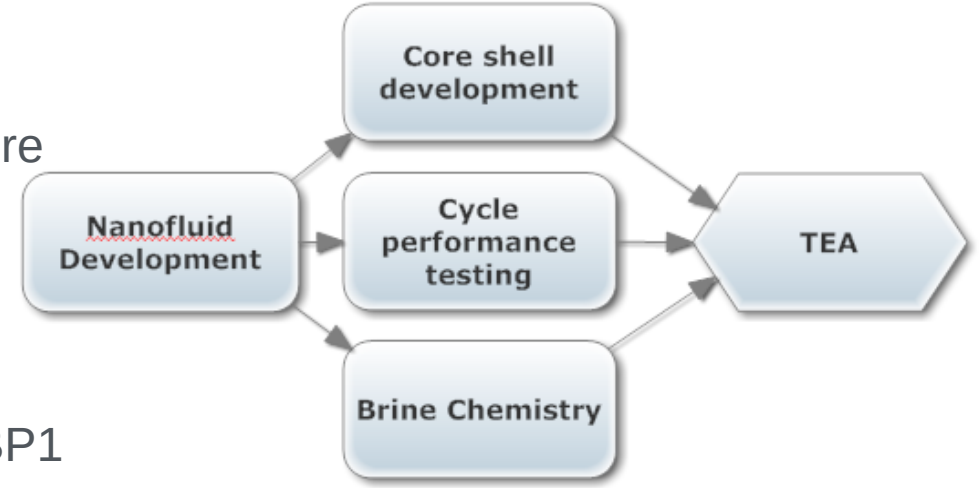
Scientific/Technical Approach

Budget Period 1



- Parallel sorbent development and testing path lowers risk of not finding effective REE extraction material
- Downselection in BP2 focuses cycle performance, stability, and magnetic core shell development work on most promising sorbent
- Techno-economic analysis updated throughout project for sorbent selection and go/no-go decision point at end of BP1

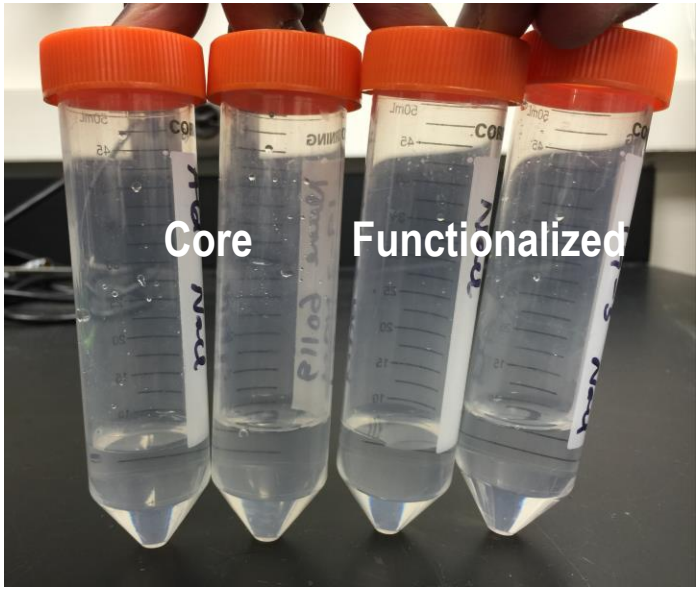
Budget Period 2



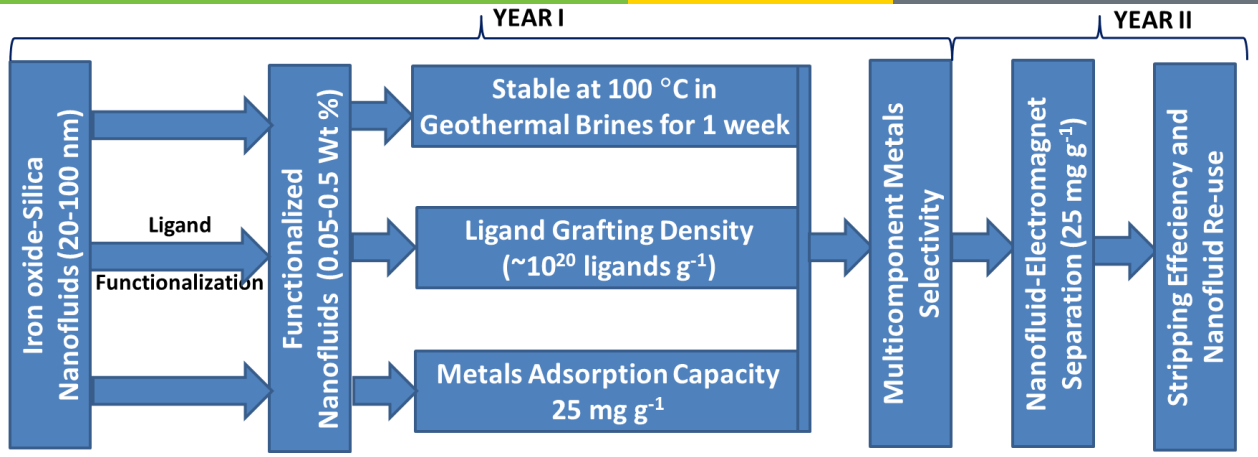
Key Technical Challenges/Questions

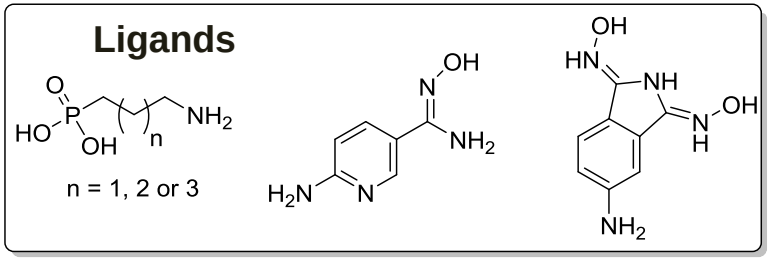
- Achieve chelating ligand density on nanoparticle surfaces of at least 10^{20} ligands per gram
- Demonstrate dispersion stability in geothermal brines of various ionic strength
- Successfully grow sorbent substrate on iron oxide core
- Show nanoparticle lifetimes of 5000 h or greater
- Demonstrate REE removal of 80% or better with exposures of 1 minute or less to functionalized nanoparticles.

Stable Dispersions of Functionalized Silica Nanoparticles

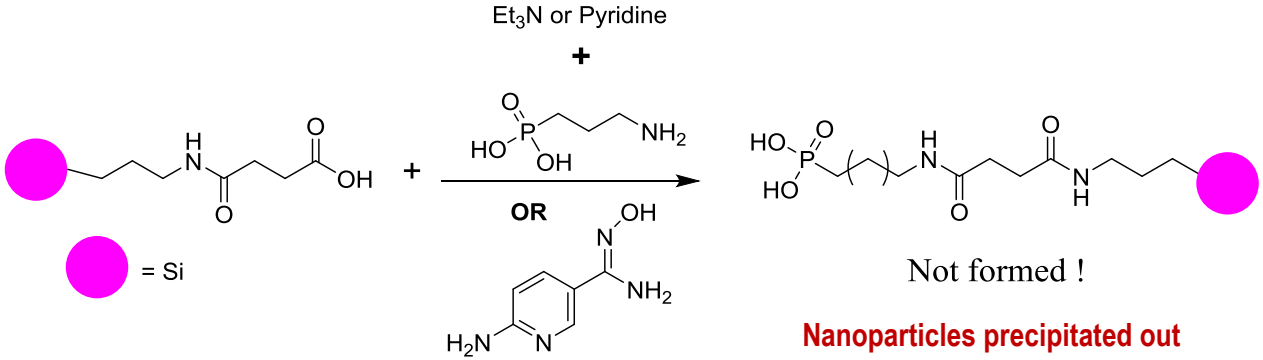


Functionalization of Silica



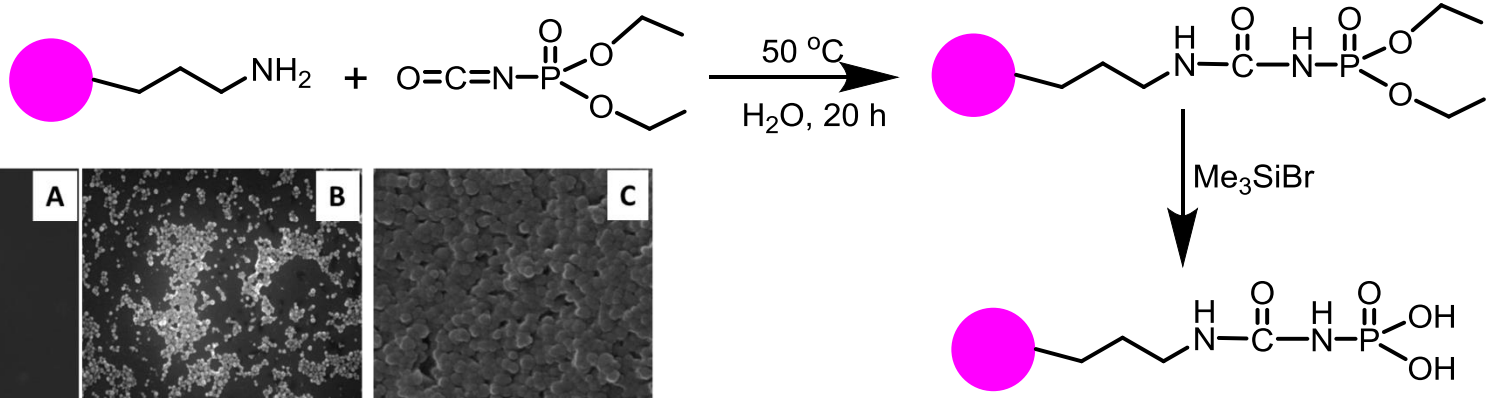


- Surface functionalization of silica nanoparticles is needed to make them suitable to extract rare earth elements (REE) from geothermal brines.
- Recent study on uranium capture from sea water proved that one organic ligand (amidoxime derivatives) might not be enough to selectively extract/ capture critical metals from geothermal brines.

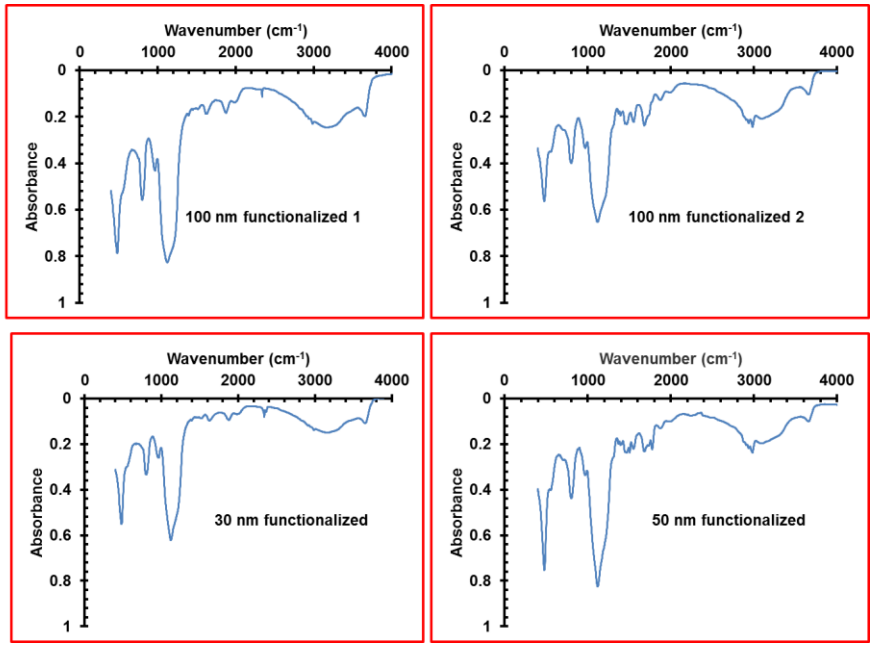


- Presence of hydroxy functionalities on both reactants complicated the reaction.
- Developed an approach for activating acid functionalized silica

Functionalization of Silica



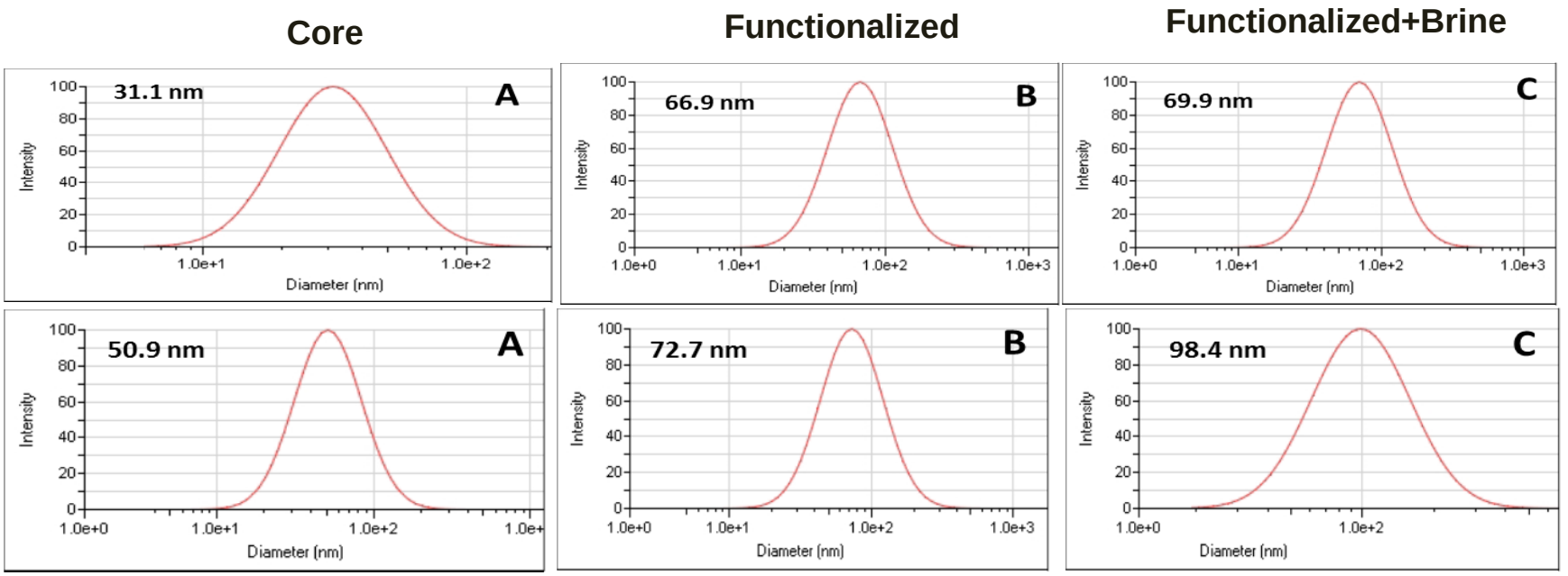
100 nm 30 nm 50 nm



- Successfully functionalized 30 and 50 nm core silica nanoparticles with diethoxy phosphinyl isocyanate in water
- Functionalization of 100 nm silica under identical conditions experienced stability issues in water and ethanol
- IR spectroscopy of functionalized silica confirms the presence of bands in the region (1650-1800 cm^{-1}).

Functionalization of Silica: Stability

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

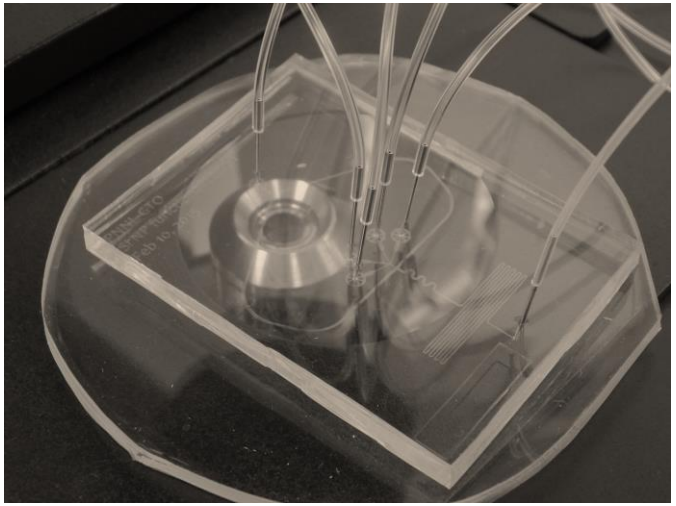


- We studied the stability of functionalized nanoparticles in brine (6 wt% NaCl)
- Colloidal stability was tested by challenging nanoparticles with stock solutions of NaCl
- The stability of the functionalized nanoparticles in brine was evaluated by using DLS measurements at room temperature.
- The functionalized nanoparticles upon exposure to brine demonstrated excellent stability confirmed by DLS measurements.
- Long term stability tests and at elevated temperatures are under investigation.

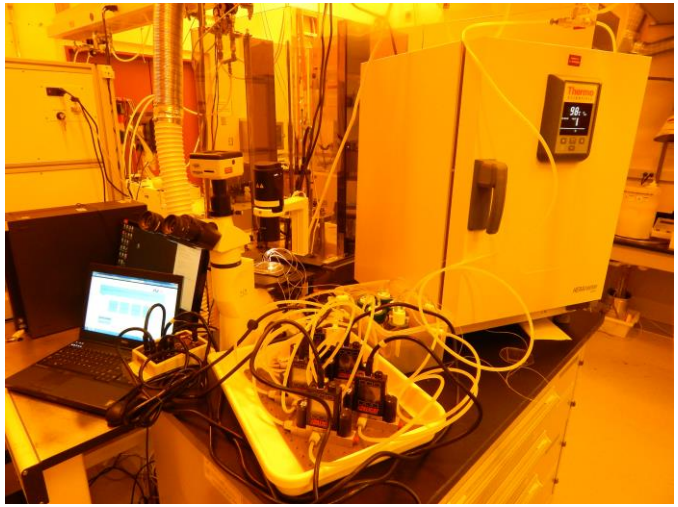
Microfluidic Reactor System

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

PDMS-based Chip



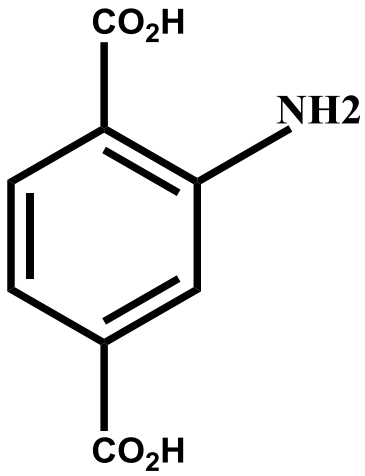
Microfluidic Setup



Teflon Chip

- Multi-ligand functionalization in single pass
- Simple and low cost process scale-up
- In early stages of application for silica functionalization – leveraging EMSL photolithography cleanroom & equipment
- Built microfluidic droplet chips that work on principle of flow focusing geometry
- Have already tested dozens of reactor designs
- Chips were fabricated with PDMS and Teflon to handle any chemical environment.

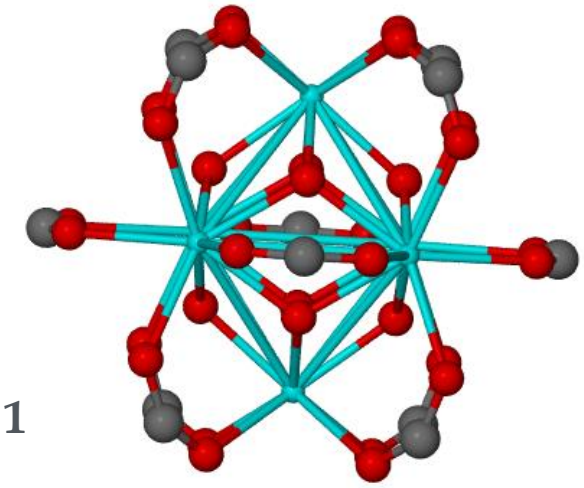
Synthesis of UIO-66 (NH_2) MOF



$ZrCl_4$ / Dimethyl Formamide

Con. HCl

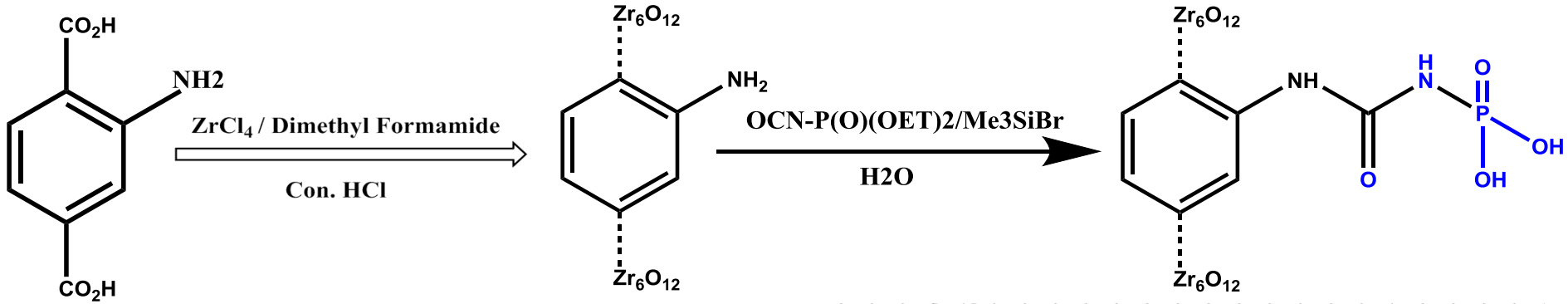
Ligand to Metal salt ratio: 1 to 1

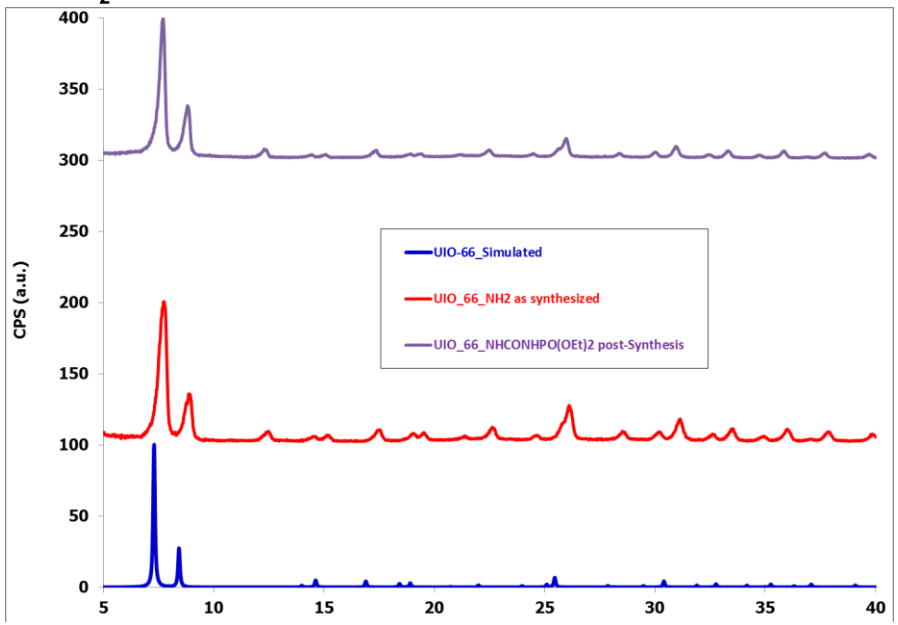


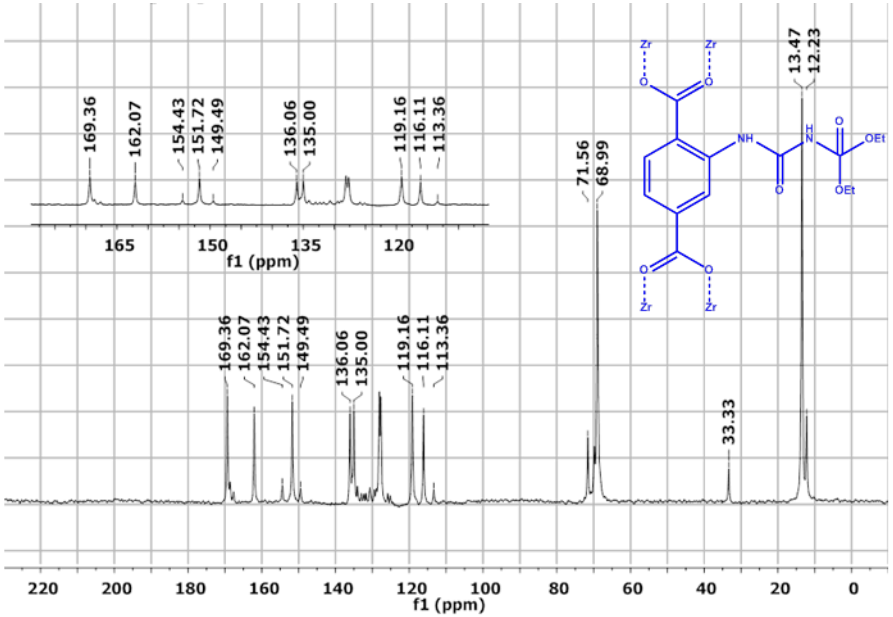
SBU of UIO-66
Zr_6 cluster

- Successfully synthesized 1 gram of UIO-66 (NH_2)
- Simulated and Experimental PXRD confirm the stability and purity of UIO-66 NH_2
- BET surface area matches with reported in the literature
- Starting material for post-synthetic functionalization route

Post-synthetic modification of UIO-66 NH_2

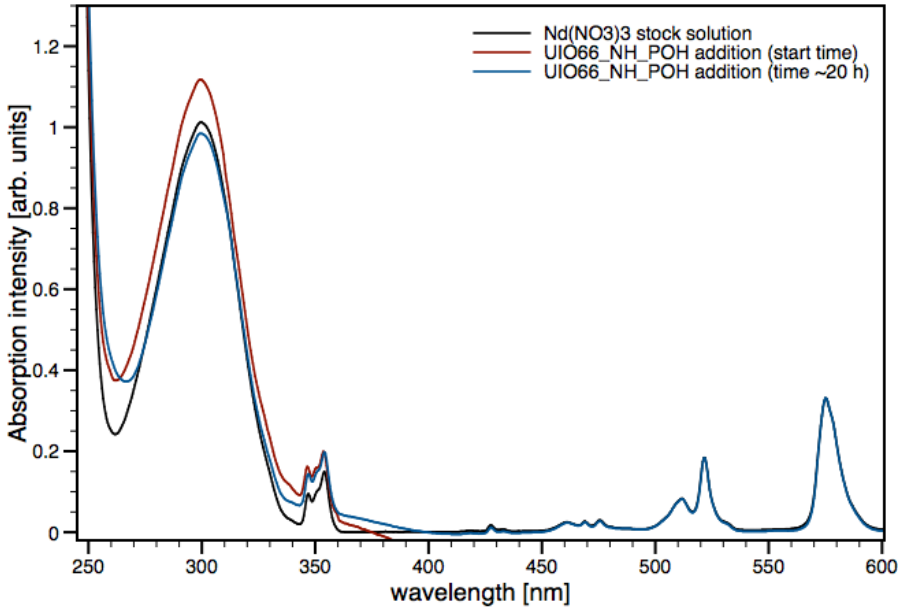


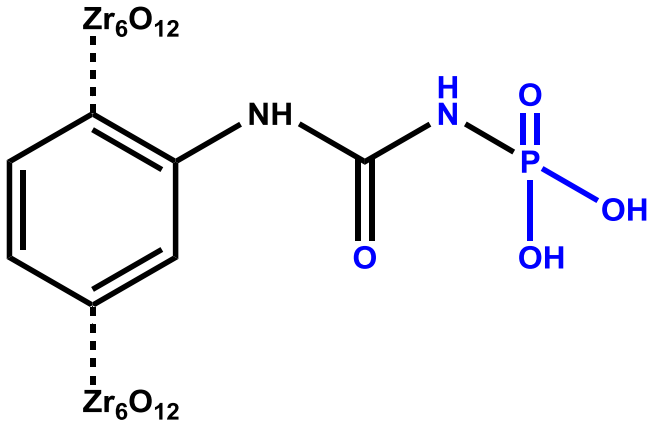




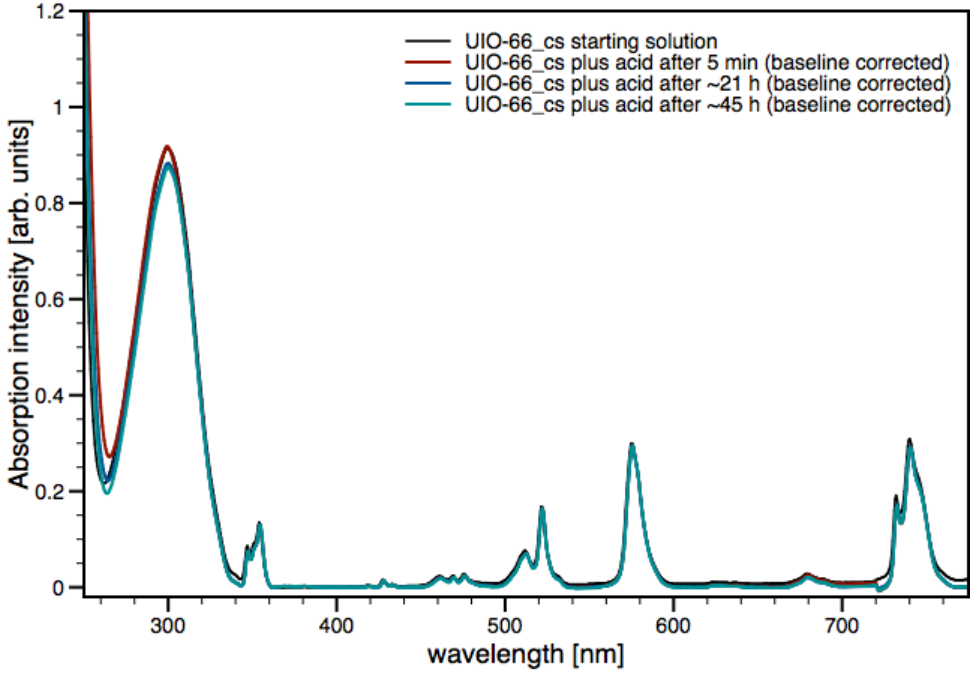
- PXRD and ^{13}C NMR of confirms the successful synthesis of phosphorylurea functionality on UIO-66.
- The NMR peaks at 10 to 80 ppm and 150 to 155 ppm corresponds to –OET and keto group
- PXRD further confirms the identical topology; IR confirms the presence of $PO(OH)_2$ stretching.

UV Absorbance for Nd Extraction Monitoring with Functionalized MOF





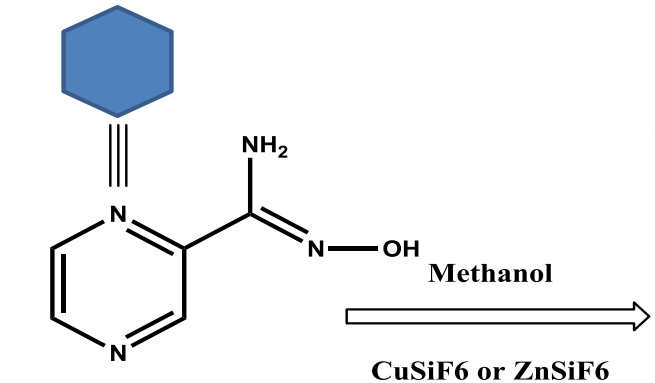
- No decrease in absorption upon adding MOF
- Quite abnormal given the free chelating sites on the surface
- Performed UV abs without Nd. The MOF UV absorbance tend to appear in the same region.



Path Forward

- Experiments are in progress by filtering out the MOF particles
- ICP-OES and MS are in progress

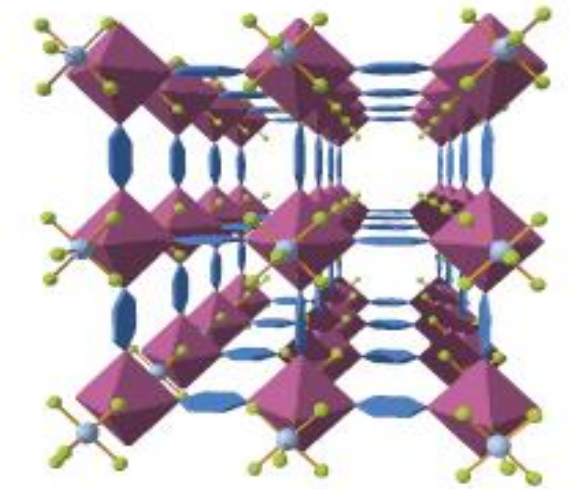
Amidoxime Functionalized MOFs



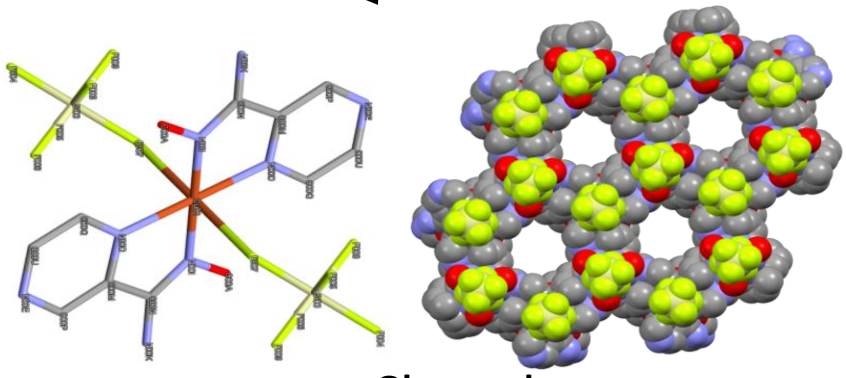
Pyrazine-2-amidoxime

Methanol

CuSiF6 or ZnSiF6

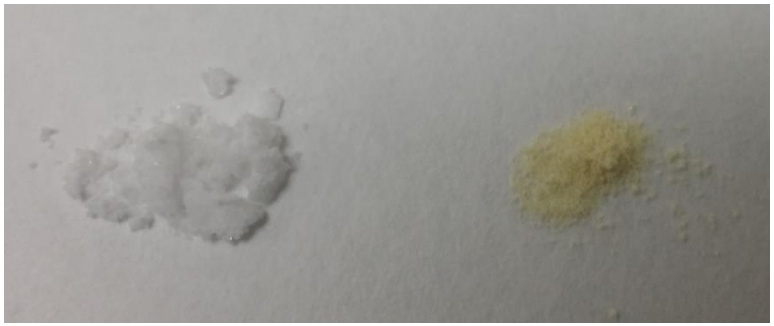


Expected



Observed

- Single Crystal X-ray shows unexpected layered structure
- Experiments are in progress to obtain the expected structure with amidoxime groups aligned in the pore surface



Future Directions

- Multifunctional silica (containing phosphonic acid and amidoximes) will be synthesized using batch and as well microfluidic approach.
- Quantify the grafting ligand density
- Perform stability studies with both silica and MOF sorbents in synthetic geothermal brine
- Complete sorption capacity measurements on selected sorbents (25-50 mg/g)
- Continue MOF synthesis trials via pre- and post-functionalization routes
- Continue experiments on removal of REE's from geothermal brine solution with various functionalized MOFs
- Complete TEA analysis for go/no-go decision at end of BP1 (end of CY)

Summary Slide

- Project is on track in terms of spending and milestone schedule
- Functionalized MOF synthesis has proved more challenging than expected
  - But ligand grafting tests are in progress to overcome this problem
- Stable dispersions of nano-functionalized silica were obtained and at much higher concentrations than originally proposed
- REE extraction testing will be the focus in upcoming quarters

Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
1. Demonstrate stable dispersion of functionalized silica sorbent in synthetic geothermal brine at mass loading of ≥0.05 wt%.	We successfully synthesized two stable dispersions of functionalized silica at mass loading of [>0.3-0.5 Wt % (based on silica)].	